

PATENT SPECIFICATION

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(54) SOLID ELECTROLYTE THIN FILM OXYGEN SENSOR

(71) We, NISSAN MOTOR COMPANY, LIMITED, a corporation organized under the laws of Japan, of No. 2, Takaramachi, Kanagawa-ku, Yokohama City, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an oxygen sensor which is in principle an oxygen concentration cell having a solid electrolyte layer and useful for detecting oxygen content in gases and liquids, particularly in exhaust gases of internal combustion engines.

Oxygen sensors of this type are of practical use for detecting oxygen content in, for example, molten metals and combustion engine exhaust gases, and the use for the measurement of oxygen content in the exhaust gases of automotive internal combustion engines is extending due to the importance of the measurement to the maintenance of the cleanness of the exhaust gases at a desirable level.

In conventional oxygen sensors of this type for use in automotive engine exhaust systems, a solid electrolyte layer as the principal component of each sensor has in most cases the shape of a tube which is closed at its one end as shown, for example, in U.S. Patent 3,960,693 for the convenience of attaching the sensor to either an exhaust manifold or an exhaust pipe such that the electrolyte layer is exposed at its one side (the outside of the tube) to the exhaust gas and at the other side to a reference gas, i.e. an oxygen-containing gas typified by air. The outer and inner surfaces of the solid electrolyte tube are coated with porous and electron conductive layers such as of platinum respectively as the anode and cathode electrodes of an oxygen concentration cell. The solid electrolyte is partly received in a tubular metal shell such that a closed end portion of the tube

protrudes from the shell and that the outer electrode layer makes an intimate contact with the inside of the shell. The outside of the solid electrolyte tube and the inside of the shell have radially enlarged portions to achieve a tight fitting. Usually a tubular metal member is fixedly inserted into the solid electrolyte tube from its open end so as to function both as an electrode member and as an air-admitting port.

As a practically serious disadvantage of such design, the fabrication of the solid electrolyte tube, which is not uniform in diameter and has a closed end, needs complicated procedures. Besides, the shell too must have a complicated shape, and a great care must be taken of the electrical connection of the conductive layers on the electrolyte tube with the shell and the inner electrode member. In a differently designed oxygen sensor of the same principle as shown in U.S. Patent 3,940,327 for example, a solid electrolyte layer takes the form of a disc and is fixedly disposed in an end portion of an open-ended tubular shell. This design also involves a complicated shape of the shell and troublesomeness of the electrical connection.

The troubles with the design and fabrication of the above described conventional oxygen sensors originate from that the solid electrolyte is a hard-to-machine ceramic material (a metal oxide system) but nevertheless needs to be formed into either a tube or a plate of a specific shape so as to be exposed to an exhaust gas stream at its one side and to a reference gas at the other side. Because of being a ceramic material, there is a great limitation on the shape and dimensions, particularly thickness, of the solid electrolyte member in the sensor. In addition the solid electrolyte member is not sufficiently resistant to thermal and mechanical shocks, so that the provision of a protection means is in many cases needful.

It is another disadvantage of the above described oxygen sensors that there occurs

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a considerable lowering in the output voltages of the sensors when used at not sufficiently high temperatures. This problem is serious to oxygen sensors for use in automotive exhaust systems since the exhaust gas temperature exhibits a considerable variation depending on the operating condition of the engine. The exhaust gas temperature becomes lowest under idling condition: it remains as low as about 250°C. As is known solid electrolyte oxygen concentration cells cannot operate at temperatures below a certain level, and a temperature of 250°C is not well above such a level. Practical oxygen sensors for automotive exhaust systems are designed such that a sensible portion of the solid electrolyte tube or disc can be positioned in the exhaust manifold or exhaust pipe at a sufficient distance from the wall of the manifold or pipe, despite inconvenience to the fabrication, with the intention of maintaining the sensitive portion at temperatures as high as possible, but the effect is limited.

When an oxygen sensor, i.e. an oxygen concentration cell, is exposed at one side of its solid electrolyte layer to a gas such as an engine exhaust gas whose oxygen partial pressure is P_1 , and at the other side to a reference gas such as air whose oxygen partial pressure is P_2 , the cell develops theoretically an electromotive force E between the two sides of the electrolyte layer determined by the Nernst equation:

$$E = \frac{RT}{4F} \log_e \frac{P_1}{P_2} \quad (1)$$

where R is the gas constant, T represents absolute temperature, and F is the Faraday constant.

A practical output voltage V of the cell differs from the potential E since the cell has an internal resistance R_1 and the potential E is detected by means of an instrument having an input resistance R_2 . The practical output voltage V is given by

$$V = \frac{E \cdot R_2}{(R_1 + R_2)} \quad (2)$$

The solid electrolyte in the cell has such a great resistivity that the internal resistance R_1 of the cell can be regarded nearly equal to the resistance r of the solid electrolyte layer, given by

$$R = (l/\rho) \cdot (t/S) \quad (3)$$

where ρ is the conductivity of the solid electrolyte, t is the thickness of the solid electrolyte layer and S is an effective

surface area of the same layer. The conductivity ρ usually varies according to the following equation:

$$\rho = \rho_0 \exp(-Q/RT) \quad (4)$$

where ρ_0 is a constant specific to each material, Q is another constant which is specific to each material and implies an activation energy for diffusion of ions, and both R and T represent the same as in Equation (1).

Equation (2) indicates that the output voltage V can be raised either by using a potential detection instrument having a large input resistance R_2 or by lowering the internal resistance R_1 of the cell (i.e. the resistance r of the solid electrolyte layer). However, it is practically difficult to greatly increase the input resistance R_2 of the detection instrument from a commonly employed 0.1—1 MΩ level and is even unfavourable from the viewpoint of avoiding the influence of noise. The internal resistance R_1 of the cell will be lowered by the following measures.

(a) The use of a solid electrolyte material having a large value for the constant ρ_0 and a small value for the constant Q .

(b) A decrease in the thickness t of the solid electrolyte layer.

(c) An increase in the surface area S of the solid electrolyte layer.

(d) The use of the cell in an atmosphere maintained at a high absolute temperature T .

The measure (d) is impractical when the cell is used for detecting oxygen content in a relatively low temperature gas such as the exhaust gas during idling of the engine. The measures (a), (b) and (c) are worthy of serious considerations but encounter the following problems.

(a) At present there is no solid electrolyte material which is of use in severe environments such as exhaust gas streams of automotive internal combustion engines and has a sufficiently large conductivity.

(b) It is practically impossible to produce a solid electrolyte layer having a thickness smaller than 0.5—1 mm by a commonly employed production method in which a powdered solid electrolyte material is molded (in either dry or wet state) and then sintered, sometimes followed by machining. The product inevitably involves cracks and/or holes if the thickness is further decreased.

(c) An increase in the surface area S of the solid electrolyte layer means an enlargement of the size of the oxygen sensor. This is contrary to an earnest demand for a compact oxygen sensor.

It is quite difficult, therefore, to improve the low temperature characteristics of

conventional solid electrolyte oxygen sensors which utilize a solid electrolyte layer in the form of a structural member.

5 It is an object of the present invention to provide an improved oxygen sensor which utilizes an oxygen ion conductive solid electrolyte as convention oxygen sensors but can develop sufficiently high voltages even at relatively low temperatures
10 experienced in exhaust gases of automotive internal combustion engines.

It is another object of the invention to provide an improved solid electrolyte oxygen sensor which comprises a source of
15 a reference oxygen partial pressure in the form of a solid mass and can be fabricated in a compact and mechanically strong construction.

It is a still another object of the invention to provide a solid electrolyte oxygen sensor in which a solid electrolyte takes the form of a thin film.

The present invention consists in an oxygen sensor or an oxygen concentration cell type, comprising:

25 a solid body made of a compacted powder mixture of a metal and an oxide of said metal, said mixture serving as the source of a reference oxygen pressure, said body serving as a basic structural support member in the oxygen sensor and having first and second portions different in dimensions;

30 a thin film of an oxygen ion conductive solid electrolyte coated on a surface of said first portion of said body so as to leave an uncoated surface to said second portion;

35 an electron conductive and gas permeable layer coated on said thin film;

40 a metal casing which encases the larger one of said first and second portions of said body and has a first opening to leave at least a major portion of said conductive and gas permeable layer open to an external atmosphere and a second opening permitting electrical connection to said uncoated surface; and

45 an insulating layer interposed between said body and said casing such that the inside of said casing is partially in contact with said conductive and gas permeable layer but is isolated from said uncoated surface.

50 A Ni—NiO system is the most preferred example of the material of the body. Any of conventional oxygen ion conductive solid electrolytes are useful as the material of the electron conductive layer.

55 In this oxygen sensor, the metal-oxide body serves also as a mechanically basic member of the sensor and can take a shape convenient for both production and use of the sensor such as the shape of the generally cylindrical rod or a disc. The solid electrolyte thin film can be formed by
60 application of a powdered material directly

onto the surface of the body and is allowed to have a very small thickness such as 1—200 μm since the film is supported by the body and does not need to serve as a structural member. Accordingly, this oxygen sensor provides sufficiently high output voltages even when used at relatively low temperatures as in the case of oxygen concentration detection in the exhaust gas of an automotive internal combustion engine under idling condition. Because of simplicity of construction and absence of any hollow portion (there is no need of admitting reference gas), this oxygen sensor can be produced with greater ease and at less costs compared with conventional solid electrolyte oxygen sensors and has an improved reliability.

The metal-oxide body in this oxygen sensor serves as the cathode of the oxygen concentration cell and, in practical applications, would be partly encased in a metal casing together with a lead to be connected to the conductive layer coated on the body. The metal casing too can take a relatively simple shape.

Figure 1 is a longitudinal sectional view of an oxygen sensor as an embodiment of the invention;

Figure 2 is an enlargement of a part of Figure 1;

Figure 3 is a longitudinal sectional view of a differently shaped oxygen sensor as another embodiment of the invention;

Figure 4 is an enlargement of a part of Figure 3;

Figure 5 shows a laboratory equipment used for testing the ability of the sensors of Figures 1 and 3;

Figure 6 is a graph showing the relationship between the air/fuel ratio of a combustible gas mixture and the output voltage of the sensor of Figure 1 exposed to the exhaust gas of the combustible mixture; and

Figure 7 is a graph showing the dependence of the output voltage of the sensor of Figure 1 on the thickness of a solid electrolyte coating which is a component of the sensor.

As an embodiment of the invention, an oxygen sensor 10 of Figure 1 has a generally cylindrical body 12 which occupies a major portion of the sensor 10. This body 12 is a solid mass of a mixture of a metal and an oxide of the same metal and serves both as a mechanically basic member of the sensor 10 and as a source of a reference oxygen partial pressure needful to the sensor 10. In the illustrated case the body 12 consists of a relatively thin and elongate portion 12a to be disposed in a gas subject to measurement, a radially enlarged portion 12b which occupies an end portion of the body 12 for the convenience of constructing

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the sensor 10 and a tapered portion 12c as a mid-portion between the thin and thick portions 12a and 12b. Figure 2 presents an enlarged detail of the sensor 10 in a region indicated at A in Figure 1. The body 12 is intimately laid with a thin layer 14 of an oxygen ion conductive solid electrolyte except the thick portion 12b (at least an end region of this portion 12b). An electronically conductive and gas permeable layer 16 is laid on the solid electrolyte layer 14. The end face of the thick portion 12b of the body 12 is covered with an insulating layer 18 of a heat-resistant material, and a metal pin or wire 20 serving as a lead is embedded or stuck into the body 12 from the end face of the thick portion 12b in the axial direction. The lead 20 outside the body 12 is jacketed with a heat-resistance insulator 22 and fixed to the body 12 by screwing and/or soldering. A wire clot 24, which serves as another lead of the sensor 10, is arranged to sheath the insulator 22 and the peripheral surface of the thick portion 12b of the body 12. The wire cloth lead 24 is held against the surface of the body 12 and electrically connected with the electronically conductive layer 16 by inserting the body 12 together with the wire cloth lead 24 in a funnel-like casing 26 of a metal plate such that the tapered portion 12c of the body 12 is supported by a tapered end portion of the casing 26 and circumferentially crimping the other end portion of the casing 26 so as to forcibly interpose or clamp the wire cloth 24 between the inside of the casing 26 and the peripheral surface of the thick portion 12b of the body 12. The casing 26 may be provided with screw threads on its outside for attachment of the sensor 10 to, for example, an exhaust pipe. Optionally the conductive layer 16 may be laid with a porous layer 28 of a chemically stable and heat-resistant material for protection purposes.

The fabrication of this oxygen sensor 10 is quite easy compared with conventional oxygen sensors having a tubular member of a solid electrolyte. Since the material of the body 12 comprises a metal component other than a metal oxide component, it is feasible to machine the material into the body 12 of desired shape and size with high precision, while commonly used solid electrolytes are typical ceramic materials and hence cannot readily be machined. The body 12 can be drilled and is electronically conductive (serves as an electrode member), so that the joining of the lead 20 to the sensor 10 can be achieved easily and reliably by screwing and/or soldering.

The material of the solid electrolyte layer 14 is selected from known oxygen ion conductive solid electrolytes such as ZrO_2

with the addition of a stabilizing oxide such as CaO , Y_2O_3 , SrO , MgO or ThO_2 ; Bi_2O_3 stabilized with Nb_2O_5 , SrO , WO_3 , Ta_2O_5 or Y_2O_3 ; ThO_2 - Y_2O_3 system and CaO - Y_2O_3 system. The solid electrolyte layer 14 can be formed by a sputtering technique, plasma spraying or sintering of a powdered material applied onto the surface of the body 12 as a dispersion in a liquid.

Examples of (metal)-(metal oxide) mixtures useful as the material of the body 12 are Ni - NiO , Cd - CdO , Zn - ZnO , Cu - Cu_2O , Co - CoO and Cr - Cr_2O_3 with various metal percentages ranging from 1 to 99 Wt%. The use of a Ni - NiO mixture is the most preferable. The body 12 is produced usually through the procedures of molding a powder mixture into a compacted mass of a suitable size, sintering the mass in an inert atmosphere and machining the sintered mass.

The outer electrode layer 16 is similar to that of the hereinbefore described conventional oxygen sensors both in material and in production method. When the electrode layer 16 is desired to exhibit no catalytic activity on the oxidation of hydrocarbons and carbon monoxide, Ag , Au or SiC may be used as the material. When the electrode layer 16 is desired to be catalytic for the oxidation, the material is selected from the platinum group metals, i.e. Ru , Rh , Pd , Os , Ir and Pt , including their alloys, and alloys of a platinum group metal and a base metal. The electrode layer 16 is formed either by a sputtering technique or by firing a metal-powder paste applied onto the surface of the solid electrolyte layer 14.

The insulating layer 18 and the insulating jacket 22 are of, for example, alumina, mullite, aluminosilicate, forsterite or spinel.

The material of the casing 26 is usually a corrosion-resistant alloy typified by stainless steel such as AISI 304 or 430 stainless steel.

Copper, brass and stainless steel are examples of the materials of the leads 20 and 24. The inner lead 20 may be omitted by shaping the end portion of the body 12 so as to serve as an electrical terminal.

The material of the protective coating 28 is usually an oxide such as alumina, beryllia or zirconia, a carbide such as silicon carbide, a nitride or a boride.

Figure 3 shows an oxygen sensor 100 as another embodiment of the invention. This oxygen sensor 100 is principally similar to the sensor 10 of Figure 1 but has a different shape. In this sensor 100 a body 112, which is a solid mass of one of the above-described (metal)-(metal oxide) mixtures capable of developing a reference oxygen partial pressure, takes the form of a disc in its major portion 112a and has a cylindrical projection 112b of a smaller diameter on

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one side of the disc portion 112a. As seen in Figure 4 which is an enlargement of a part (indicated at B) of Figure 3, the flat side of the disc 112a is entirely laid with a thin electrolyte layer 114 (the peripheral surface of the disc 112a too may be laid with this layer 114 either partly or entirely) and an electron conductive and gas permeable layer 116 is formed intimately on the solid electrolyte layer 114. The other side of the body 112 except the projection 112b is covered with an insulating layer 118. A metal casing 126, which originally has the shape of a cup with a wide opening at the bottom, receives therein the disc portion 112a of the body 12 such that the conductive layer 114 makes an intimate contact with the inside of the casing, and an upper end portion of the casing 126 is circumferentially crimped so as to interpose and clamp the insulating layer 118 between the crimped portion and the end face of the disc portion 112a. The projection 112b is so small in diameter relative to the disc portion 112a that the crimped casing 126 does not come into contact with the projection 112b. A porous protection layer 128 may optionally be formed on the conductive layer 114 over an area left exposed through the opening of the casing 126. The materials for this sensor 100 are not different from those for the sensor 10 of Figure 1.

In this oxygen sensor 100 the casing 126 is utilized as one electrode member and the projection 112b of the metal-containing body 112 is designed to serve as the other electrode member.

A resilient material such as a corrugated spring sheet or a leaf spring may be interposed between the insulating layer 118 and the body 112 with the purpose of protecting the body 112 against breakage by mechanical vibrations or thermal expansion.

The invention will be further illustrated by the following examples.

EXAMPLE 1

This example relates to the oxygen sensor 10 of Figure 1. The starting material of the body 12 was a mixture of Ni powder (44 Wt%) and NiO powder (56 Wt%). This powder mixture was molded under a pressure of 500 kg/cm² into a disc of 50 mm in diameter and 20 mm in thickness, and the disc was sintered in nitrogen atmosphere at 1200°C for 1 hr. The sintered disc had a compression strength of 800 kg/cm². The body 12 was produced by machining the sintered disc. The diameter of the body 12 was 1.5 mm in the thin portion 12a and 3 mm in the thick portion 12b. The body 12 had a total length of 14 mm: the thin portion 12a and the thick portion 12b were respectively 10 mm and 3 mm in length. A

hole of 1 mm in diameter was drilled in the thick portion 12b from its end face and a female screw was cut on the wall of the hole. A screwed pin of AISI 304 stainless steel was fitted in this hold and soldered as the cathode lead 20.

A powder mixture (0.5–30 μm in particle size) of 85 mol% Bi₂O₃ and 15 mol% Nb₂O₅ was used as the raw material of the solid electrolyte film 14, and the film 14 was formed in five different ways.

1-A. The solid electrolyte powder was dispersed in water to give a slurry containing 50 Wt% water. The thin portion 12a and the tapered portion 12c of the body 12 were immersed in this slurry. By firing the body 12 with the solid electrolyte coating (after air-drying) in air at 920°C, the wet coating turned into a ceramic thin film whose thickness was about 50 μm.

1-B. The immersion of the body 12 in the above described slurry and subsequent air-drying were cycled three times. Thereafter the same firing as in 1-A was carried out with the result that the ceramic solid electrolyte film 14 was about 150 μm thick.

1-C. The above described slurry was diluted with water such that the water content became 80 Wt%. The diluted slurry was sprayed on the surface of the body 12 with a hand sprayer. After air-drying, firing was carried out under the above described condition. The thickness of the solid electrolyte film 14 was about 10 μm in this case.

1-D. The powder mixture of 85 mol% Bi₂O₃ and 15 mol% Nb₂O₅ was molded into a disc of 30 mm in diameter and 1 mm in thickness and sintered in air at 920°C. The coating of the Ni–NiO body 12 with the solid electrolyte was performed by a high frequency sputtering technique using the Bi₂O₃–Nb₂O₅ disc as the target. The sputtering was continued for 20 min. Then the coated body 12 was fired in air at 920°C for 20 min. The resultant ceramic solid electrolyte film 14 was about 1 μm thick.

1-E. The procedures of 1-D were repeated except that the sputtering was continued for 200 min. In this case the thickness of the ceramic solid electrolyte film 14 was about 10 μm.

The five kinds of solid electrolyte films 14 were each coated with a porous platinum layer (the electron conductive layer 16) by the following method. A platinum black powder having a mean particle size of 2 μm was prepared by reduction of chloroplatinic acid dissolved in water with the addition of hydrazine hydrate. A dispersion of this platinum black powder in a nitrocellulose lacquer was sprayed on the surface of the solid electrolyte film 14 with a hand sprayer. To leave the thick portion 12b of the body 12 uncoated with platinum, the thick

portion 12b was masked in its end face and a major portion of the peripheral surface over a length of 2 mm from the upper end. The wet platinum coating was dried at 80°C and then fired at 900°C.

The porous protection layer 28 was formed on the platinum layer 16 by plasma-spraying of alumina powder to a thickness of about 50 μ m.

The thus produced five kinds of cells were assembled with a stainless steel casing 26 and a copper wire cloth as the anode lead 24, using alumina as the material of the insulators 18 and 22.

The output characteristics of the oxygen sensors produced in this example were examined by the use of a test apparatus as shown in Figure 5. A combustor 30 for burning propane gas with air had an exhaust pipe 32, which was provided with a cooling water duct 34 for regulating the temperature of the combustion gas. The oxygen sensor 10 to be tested was inserted into the exhaust pipe 32 at a sufficient distance from the combustor 30 such that the combustion gas temperature at the location of the sensor 10 could be accurately regulated. The gas temperature at this location was measured by means of a thermocouple 36. The air-to-propane ratio also was regulatable.

When the combustion gas temperature in the exhaust pipe 32 at the location of the oxygen sensor 10 was 250°C, the dependence of the output voltage V of the sensor 10 on the air-to-propane ratio (by weight) was as shown by the solid line curve in Figure 6 for the sample 1-D. The broken line curve in Figure 6 represents the same for a conventional oxygen sensor comprising a 0.5 mm thick disc of a sintered solid electrolyte (85 mol% Bi_2O_3 and 15 mol% Nb_2O_5).

At a fixed air-to-propane ratio of 17, the output voltages V of the five samples 1-A, 1-B, 1-C, 1-D and 1-E and the conventional oxygen sensor (Ref.) at 250°C were different as shown in Figure 7. This graph demonstrates a great dependence of the output voltage V on the thickness t of the solid electrolyte layer 14 and, hence, the advantage of a thin film solid electrolyte oxygen sensor according to the invention:

EXAMPLE 2.

This example relates to the oxygen sensor 100 of Figure 3. The Ni—NiO powder mixture used in Example 1 was molded and sintered to give a disc as in Example 1. The body 112 was produced by machining the sintered disc to have a diameter of 12 mm and a thickness of 1 mm in the disc portion 112a, with the cylindrical projection 112b of 3 mm in diameter and 1 mm in length.

In this example, a ZrO_2 (85 mol%)— Y_2O_3 (15 mol%) system was used as the

material of the solid electrolyte layer 114, and a sputtering technique was employed for forming this layer 114 as a thin film by the use of a molded disc of the solid electrolyte as the target. The sputtering was performed for various amounts of time such that only the non-projected end face and the peripheral surface of the disc portion 112a were coated with the solid electrolyte to various thicknesses. Then the coated body 112 was fired in air at 1100°C for 1 hr to obtain a stable and strongly adhered ceramic thin film 114 on the disc portion 112a. The electron-conductive layer 116 was formed on the solid electrolyte film 114 by the application of the platinum black lacquer as in Example 1 and a subsequent firing at 1000°C for 1 hr.

The thus produced cell was encased in the casing 126 of AISI 430 stainless steel together with the insulator layer 118 of alumina. The casing 126 was electrically in contact with the platinum layer 116 to serve as the anode electrode member of the sensor 100, while the projection 112b of the Ni—NiO body 112 served as the cathode. Thereafter the platinum layer 116 was laid with an about 50 μ m thick porous protection layer 128 of alumina by plasma-spraying.

The sensor 100 produced in Example 2 was subjected to the above described test using the apparatus of Figure 5. The sensor 100 was attached to the exhaust pipe 32 such that the combination gas streamed along the end face coated with the solid electrolyte film 114 and the platinum layer 116. When the air-to-propane ratio was 17 and the combustion gas temperature at the location of the sensor 100 was 250°C, the output voltage V of the sensor 100 was about 900 mV for a sample having an 1 μ m thick solid electrolyte film 114 and about 890 mV for another sample having a 10 μ m thick solid electrolyte layer.

For comparison, an oxygen sensor of a conventional design, comprising a 12 mm diameter and 0.5 mm thick sintered disk of a ZrO_2 (85 mol%)— Y_2O_3 (15 mole%) system held in a tubular metal shell, was tested under the same condition. The output voltage V of this sensor was only about 50 mV, so that this sensor was of little use for measurements of oxygen concentrations in an engine exhaust gas.

WHAT WE CLAIM IS:—

1. An oxygen sensor of an oxygen concentration-cell type, comprising:
 - a solid body made of a compacted powder mixture of a metal and an oxide of said metal; said mixture serving as the source of a reference oxygen pressure; said body serving as a basic structural support member in the oxygen sensor and having

first and second portions different in dimensions;

5 a thin film of an oxygen ion conductive solid electrolyte coated on a surface of said first portion of said body so as to leave an uncoated surface to said second portion;

10 an electron conductive and gas permeable layer coated on said thin film; a metal casing which encases the larger one of said first and second portions of said body and has a first opening to leave at least a major portion of said conductive and gas permeable layer open to an external atmosphere and a second opening

15 permitting electrical connection to said uncoated surface; and

20 an insulating layer interposed between said body and said casing such that the inside of said casing is partially in contact with said conductive and gas permeable layer but is isolated from said uncoated surface.

2. An oxygen sensor as claimed in Claim 1, wherein said body has the shape of a generally cylindrical rod, said first portion being a portion starting from one end of said rod, said second portion being a portion starting from the other end of said rod and larger in diameter than said first portion,

30 both said one end and the cylindrical surface of said first portion being coated with said thin film, said other end of said rod being left uncoated with said thin film.

3. An oxygen sensor as claimed in Claim

1, wherein said first portion of said body has the shape of a disc, said second portion being a projection on one side of said disc smaller in cross-sectional area than said disc, the other side of said disc being coated with said thin film.

4. An oxygen sensor as claimed in Claim 1, wherein said powder mixture is a mixture of Ni and NiO.

5. An oxygen sensor as claimed in Claim 4, wherein said body is made of a sintered mass.

6. An oxygen sensor as claimed in Claim 1, wherein the thickness of said thin film is from about 1 to about 200 μm .

7. An oxygen sensor as claimed in Claim 6, wherein said thin film is formed by firing of a powder of said solid electrolyte applied onto said surface of said body in the form of a dispersion in a liquid.

8. An oxygen sensor as claimed in Claim 6, wherein said thin film is formed by a sputtering technique using a sintered mass of said solid electrolyte as the target.

9. An oxygen sensor according to Claim 1, substantially as hereinbefore described with reference to Figures 1 and 2 or Figures 3 and 4 of the accompanying drawings.

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FIG. 1

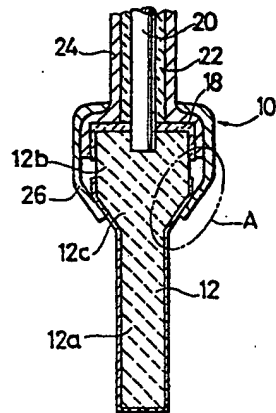
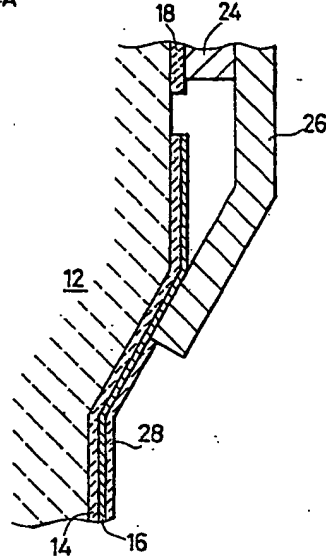


FIG. 2



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FIG. 3

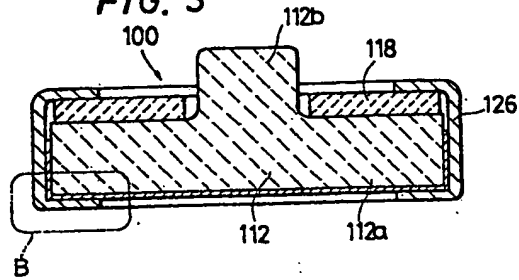


FIG. 4

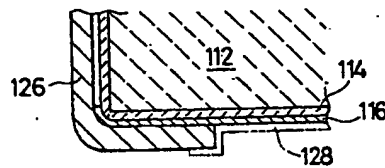
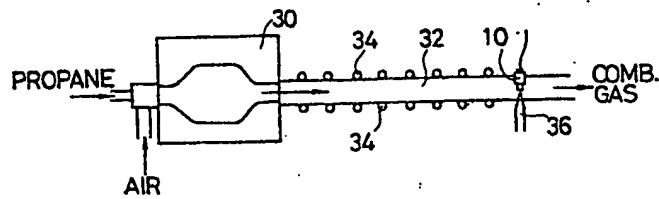


FIG. 5



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FIG. 6

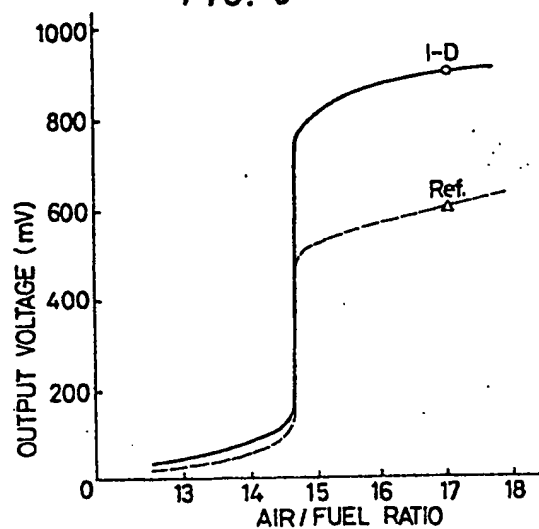
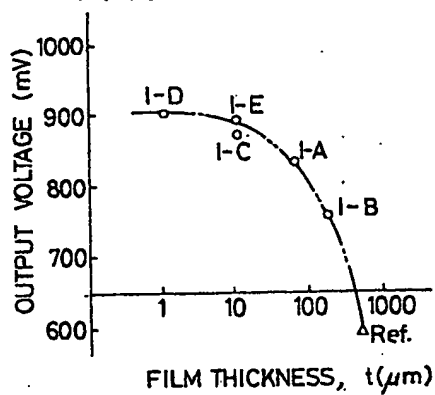


FIG. 7



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